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(54) POLYURETHANE COMPOSITION

(71) We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a new curative for polyurethane reaction mixtures. More specifically, this invention relates to a process for making polyurethanes having improved modulus at 500 percent elongation.

Recently bis(2-aminophenyl) disulfide has been used commercially to cure polyurethane reaction mixtures as it gives a satisfactory pot life. Unfortunately, the product produced by this curative has a modulus at 500 percent elongation which does not compare favorably with those produced with methylene bis-chloroaniline.

Therefore, it is an object of this invention to provide a modified bis(2-aminophenyl) disulfide curative which has satisfactory pot life and gives a polyurethane having improved modulus at 500 percent elongation.

The modified curative of this invention for a polyurethane reaction mixture which comprises a reactive hydrogen containing compound and an excess of organic polyisocyanate, or a prepolymer derived therefrom, is a curative comprising bis(2-aminophenyl) disulfide (bis-2) and a second diamine selected from the Class A consisting of 4,4'methylene dianiline (MDA), bis(4-aminophenyl) disulfide (bis-4), 1,5-diamino naphthylene (DAP) and *m*-phenylene diamine (M—PDA), said second diamine being present in an amount of 0.25 percent to 60 percent by weight, calculated on the total weight of the curative mixture, but less than the amount that exceeds its solubility in bis(2-aminophenyl) disulfide at 20°C. This curative has a pot life sufficient to permit castings to be readily made.

Although, as specified above, the modified curative of this invention contains one of the above enumerated diamines of Class A in an amount less than the amount that exceeds its solubility in the bis-2 at 20°C, it is to be understood that this does not mean that the curative is necessarily homogeneous.

Preferably the second diamine, i.e. that of Class A, is present in an amount by weight (calculated as mentioned above) of 0.25 to one percent by weight of MDA or M—PDA, 0.25 to five percent by weight of DAP, or 0.25 to 60 percent by weight of bis-4. The most preferred curative is a blend of bis-2 with 10 to 60 percent by weight of bis-4, as it gives a greater improvement in modulus at 500 percent elongation, and gives a good pot life for making castings of large sizes.

As already indicated or implied, the curative of this invention can be used in either one-shot or prepolymer methods to form polyurethanes. The curative is utilized to react with the excess of the organic polyisocyanate relative to the reactive hydrogen-containing compound. The reaction can be performed at the usual temperatures from below room temperature to above.

The nature of this invention can be more readily understood from the illustrative and representative example wherein all parts and percentages are by weight unless otherwise indicated.

EXAMPLE.

A prepolymer was made by adding 10 parts of an alkylated phenolic antioxidant to a blend of 700 parts of a 2000 molecular weight polytetramethylene glycol and 300 parts of a 1000 molecular weight polytetramethylene glycol, and then reacting at 70°C with 326 parts of 3,3' - dimethyl - 4,4' - diisocyanatodiphenyl (also called TODI). Then this prepolymer was divided into 100

part aliquots. Each aliquot was mixed with 10 parts of an amine curative and cast into physical test sheets which were cured at 70°C for 16 hours before being tested.

The physical test results on these samples are shown below for the amount of a specific curative used.

Curative Blend Ingredient, % Bis-2	DAP	Bis-4	Modulus 500% PSI	Ultimate Tensile PSI	Elongation %	Compression Set, %
100	0	0	2960	6070	660	33
95	5	0	4300			
90	0	10	3880	7720	570	28
80	0	20	4160	7400	565	26
70	0	30	4310	7050	550	25
60	0	40	4850	7400	530	26
50	0	50	6300	7520	525	21
40	0	60	6400	7220	575	25

The data in the above table show that the blend of bis-2 with the second diamine appreciably improves the physical properties of the cured polyurethanes.

In the above example the curatives are shown with a representative blend of reactive hydrogen containing compounds having molecular weights (2000 and 1000) which fall within the range of 500 to 6500. It should be indicated that instead of the polytetramethylene glycols, any of the other polyether polyols of 2 to 8 hydroxyls could be used. For example, polypropylene ether glycol could be used in the above example to obtain the benefit of the curative blend of the invention. Likewise, the polyester polyols obtained by reacting a polyol containing 2 to 3 hydroxyls and 2 to 20 carbon atoms with a polycarboxylic acid of 2 to 20 carbon atoms could be used equally well in the above example to obtain benefit from the curative blend of the invention. To be more specific, polyesters such as polyethylene adipate, polytetramethylene azelate or aromatic polyesters can be used instead of polytetramethylene glycol.

The example utilized TODI to make the prepolymer, but any of the organic polyisocyanates can be used. Representative examples of these useful organic polyisocyanates are toluene diisocyanate, methylene bis (phenylisocyanate), sometimes called MDI, and hydrogenated MDI. Generally, the reactive hydrogen containing compound and organic polyisocyanate can be used in any ratio, the ratio of 1.1 to 3.5 by weight being preferred, provided that in any case an excess of organic polyisocyanate is employed, as specified earlier.

WHAT WE CLAIM IS:—

1. A curative for a polyurethane reaction mixture which comprises a reactive hydrogen containing compound and an excess of organic polyisocyanate, or a prepolymer derived therefrom, said curative comprising bis (2-aminophenyl) disulfide and a second diamine selected from 4,4'-methylene dianiline, bis(4-aminophenyl) disulfide, 1,5-diaminonaphthylene and *m*-phenylene diamine, said second diamine being present in an amount of 0.25 percent to 60 percent by weight, calculated on the total weight of the curative mixture, but less than the amount that exceeds its solubility in bis (2-aminophenyl) disulfide at 20°C.

2. The curative of Claim 1 wherein the second diamine is bis (4-aminophenyl) disulfide.

3. The curative of Claim 2 wherein the second diamine is present in an amount of 10 to 60 percent by weight, calculated on the total weight of the curative mixture.

4. The curative of Claim 1 wherein the second diamine is 1,5-diaminonaphthylene.

5. A curative as claimed in claim 1, substantially as set forth in respect of any of the curative blends in the foregoing Example.

6. A process for making a polyurethane, wherein a curative as claimed in claim 1, 2, 3 or 4 is employed.

7. A process as claimed in claim 6, substantially as described in the foregoing Example.

8. A polyurethane made by a process as claimed in claim 6 or 7.

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